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(54) PRODUCTION OF TRANSPARENT CONDUCTIVE MEMBRANE LAMINATE

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a transparent conductive membrane laminate low in surface resistance and high in light transmissivity.

SOLUTION: A transparent conductive membrane laminate wherein at least a transparent high refractive index membrane layer (a) and a metal membrane layer (b) are provided on a transparent substrate (A) so that a laminated unit of b/a from the side of the substrate is provided as at least one unit is heat-treated not only to lower surface resistance but also to raise light transmissivity.

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$\frac{TiO_2}{Ag, Au, Cu}$   
 $\frac{TiO_2}{Ag, Au, Cu}$   
 $\frac{TiO_2}{glass}$

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CLAIMS

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- [Claim]
- [Claim 1] The field resistance which the transparent conductivity thin film layered product which \*\*\*\*\*s at least the laminating unit which consists a transparent high refractive-index thin film layer (a) and a metal thin film layer (b) of a substrate (A) side b/a at least one time is heat-treated, and field resistance is reduced on a transparent substrate (A), and is characterized by raising a light transmission is low, and it is the manufacture technique of the transparent conductivity thin film layered product with a high light transmission.
- [Claim 2] The manufacture technique of a transparent conductivity thin film layered product given in the claim 1 characterized by a metal thin film layer (b) being the alloy of the pure metal or two or more sorts of metals which were chosen out of the group of silver, gold, copper, palladium, and platinum.
- [Claim 3] The manufacture technique of a transparent conductivity thin film layered product given in the claims 1 or 2 which a transparent high refractive-index thin film layer (a) becomes from the oxide of an indium and tin, titanium oxide, or a zinc oxide substantially.
- [Claim 4] The manufacture technique of a transparent conductivity thin film layered product given in either of the claims 1-3 whose temperature of heat-treatment is 100 degrees C or more.
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## DETAILED DESCRIPTION

[Detailed description]

[0001]

[The technical field to which invention belongs] this invention's field resistance is low and a light transmission is related with the manufacture technique of a high transparent conductivity thin film layered product.

[0002]

[Prior art] A transparent conductivity thin film is a thin film which has conductivity, in spite of being transparent, and its intended use is broad. The example of representation is a thin film (ITO thin film) which consists of an oxide of an indium and tin, and is widely used now as a transparent electrode of display panels, such as a liquid crystal display, an electroluminescence (EL) display, and a plasma display.

[0003] In order for a needs to realize recently large-sized-izing and carrying-izing of a display panel which are increasing very much, the display device needs a raise in brightness and low-power-ization. For this purpose, as compared with the former, a visible light transmittance is high and it is asked for the transparent conductivity thin film which is low resistance. Especially the transparent conductivity thin film [ especially ] that has low resistance and high visible light-transmission nature to the organic EL element and field emission element which began to be put in practical use at last recently is useful. Moreover, recently, the needs of a transparent conductivity thin film which has low resistance and high visible light-transmission nature as a Hideaki object for an electromagnetic wave cutoff by the spread of OA equipment is increasing.

[0004] By choosing the modality and thickness of a thin film to use, the transparent conductivity thin film layered product which becomes by carrying out the laminating of a high refractive-index transparent thin film and the metal thin film can change an optical property and an electrical property freely, and can be said that it is the transparent conductivity thin film which was very excellent in the point that it can design so that it may have the optimum optical property and the optimum electrical property according to intended use. For example, having high visible light-transmission nature, and becoming the transparent conductivity thin film layered product which is low resistance is also known by optimizing the material and thickness of each thin film.

[0005] It is common that a glass plate is used as a substrate for supporting a transparent conductivity thin film. On the other hand, the study which substitutes the present glass for a macromolecule organizer is performed briskly. The point that the macromolecule moldings is excellent as compared with the glass plate is a grade which is made more thinly, which can perform the light thing to bend easily and not breaking. However, since there is a constraint by the thermal resistance of the substrate [ itself ] when using a macromolecule Plastic solid for a substrate, sufficient electrical property and an optical property cannot be acquired in many cases. For example, when forming ITO thin film, in order to reduce a specific resistance, heating \*\*\*\* is performed under conditions 200 degrees C or more, or heat treatment after \*\*\*\* is performed. However, when a macromolecule Plastic solid is used for a substrate, the electrical property and visible light-transmission nature in which heating of 200 degrees C or more is impossible in many cases, and it is chosen as compared with the case where ITO thin film is formed on a glass substrate, and deals are inferior.

[0006]

[Object of the Invention] The factor which determines the conductivity of the transparent conductivity thin film layered product which comes to carry out the laminating of a high refractive-index transparent thin film layer and the metal thin film layer on a transparent substrate is the resistance of a metal thin film layer. For example, in using silver for a metal thin film layer and setting the thickness to about 10nm, when a silver specific resistance takes into consideration that it is  $1.59 \times 10^{-6}$  (ohm and cm) grade, having field resistance of two (ohm/\*\*) grades is expected. However, the actual condition was that the value actually acquired is widely different as greatly as this value expected.

[0007] Silver is specifically used for a transparent high refractive-index thin film layer (a) at ITO and a metal thin film

layer (b). When the transparent conductivity thin film layered product which comes to carry out a laminating to the order which becomes A/a/b/a is formed on a transparent substrate (A) (a thickness a:40nm, respectively) Having the property of 90% or more of visible light transmittances is expected below b:10nm, about a:40nm, conditions from which the specific resistance of ITO becomes the minimum, and 2ohms of field resistance and \*\*. However, field resistance of the transparent conductivity thin film layered product actually formed was 6ohms / \*\* grade, and the visible light transmittance was about 88%.

[0008] When ITO thin film layer was formed by the oxygen reactive-sputtering method for using a metal for a target, field resistance of the transparent conductivity thin film layered product formed was still remarkably strong, and the actual condition was that a visible light transmittance becomes still remarkably low. Specifically in the above transparent conductivity thin film layered products, they were 12ohms of field resistance, \*\* grade, and about 80% of visible light transmittances.

[0009]

[The means for developing a technical problem] In order that this invention persons may solve the above-mentioned problem, as a result of repeating a research zealously, by being heat-treated under the temperature condition more than [ after a laminating ] fixed, it was remarkable, field resistance fell, and the transparent conductivity thin film layered product which comes to carry out the laminating of a transparent high refractive-index thin film layer and the metal thin film layer found out that permeability rose, and resulted in this invention.

[0010] Namely, this invention (1), On a transparent substrate (A), at least The transparent conductivity thin film layered product which \*\*\*\*\*s the laminating unit which consists a transparent high refractive-index thin film layer (a) and a metal thin film layer (b) of a substrate (A) side b/a at least one time It heat-treats, field resistance is reduced and it is characterized by raising a light transmission. Field resistance is low. The manufacture technique of a transparent conductivity thin film layered product that a light transmission is high, (2) The manufacture technique of a transparent conductivity thin film layered product given in (1) characterized by a metal thin film layer (b) being the alloy of the pure metal or two or more sorts of metals which were chosen out of the group of silver, gold, copper, palladium, and platinum, (3) A transparent high refractive-index thin film layer (a) substantially The oxide of an indium and tin, (1) which consists of titanium oxide or a zinc oxide, or the manufacture technique of a transparent conductivity thin film layered product given in (2) (4), The temperature of heat-treatment is related with the manufacture technique of a transparent conductivity thin film layered product given in either of (1) - (3) which is 100 degrees C or more.

[0011]

[Gestalt of implementation of invention] The manufacture technique of a transparent conductivity thin film layered product in this invention On a transparent substrate (A), at least a transparent high refractive-index thin film layer (a) and a metal thin film layer (b) It is characterized by heat-treating the transparent conductivity thin film layered product which \*\*\*\*\*s the laminating unit which consists of a substrate (A) side b/a at least one time, and as compared with the conventional manufacture technique, field resistance is remarkably low and can manufacture the transparent conductivity thin film layered product with it. [ remarkable beam-of-light permeability and ] [ high ]

[0012] The laminating configuration of the transparent conductivity thin film layered product of this invention should just \*\*\*\*\* the laminating unit of b/a at least one time on a transparent substrate (A) for a transparent high refractive-index thin film layer (a) and a metal thin film layer (b). A laminating unit is a configuration of that, as for the substrate (A), the direct laminating of the high refractive-index thin film layer (a) was carried out on the metal thin film (b) in the field of an opposite side here. In addition, the interlayer for raising the adhesion force to between this thin film layer and a substrate and among other thin film layers etc. may also be included. [ other than the above-mentioned configuration ]

[0013] An accompanying drawing has and explains this invention. Drawing 1 is the cross section showing an example of the transparent conductivity thin film layered product manufactured by this invention. On the transparent substrate (A) 30 which consists of glass or a macromolecule Plastic solid, the laminating of the transparent high refractive-index thin film layer (a) 10 is further carried out on it, and the transparent conductivity thin film layered product shown in drawing 1 is manufactured the metal thin film layer (b) 20 and by heat-treating. Even if a transparent high refractive-index thin film layer (a) is the layered product of a monolayer or two or more sorts of transparent high refractive-index thin film layers here, a metal thin film layer (b) may be the layered product of a monolayer or two or more sorts of metal thin film layers.

[0014] this invention -- an effect -- obtaining -- having -- transparent -- conductivity -- a thin film -- a layered product -- others -- a laminated structure -- an example -- concrete -- raising -- if -- drawing 2 -- being shown -- as -- being transparent -- a substrate -- (-- A --) -- 30 -- a top -- transparent -- high -- a refractive index -- a thin film -- a layer -- (--

a --) -- ten -- a metal -- a thin film -- a layer -- (-- b --) -- 20 -- transparent -- high -- Moreover, laminated-structure A / b/a/b, laminated-structure A / b / a/b/a ( [drawing 3](#) ), Laminated-structure A / a/b/a/b / a ( [drawing 4](#) ), laminated-structure A/b/a/b/a/b/a ( [drawing 5](#) ), What is necessary is to be laminated-structure A/a/b/a/b/a/b / a ( [drawing 6](#) ), laminated-structure A/b/a/b/a/b/a/b/a ( [drawing 7](#) ), laminated-structure A/a/b/a/b/a/b/a/b/a ( [drawing 8](#) ), etc., and just to include at least one laminating unit of b/a in a laminated structure. The direct laminating of the high refractive-index thin film layer is carried out to a laminating unit with a substrate (A) on a metal thin film here at the field of an opposite side.

[0015] As a material of the transparent high refractive-index thin film layer (a) used in this invention, it is desirable to excel in transparency as much as possible. Here, when the thin film of about 100nm of thickness is formed as excelling in transparency, it points out that the permeability to light with a wavelength [ of the thin film ] of 400-700nm is 60% or more. Moreover, the refractive indexes to 550nm light are 1.4 or more materials, and a high refractive index may make an impurity mix in these by intended use. Hereafter, they are illustrated.

[0016] As a material of a transparent high refractive-index thin film layer (a), it is the most desirable to use a transparent high refractive-index oxide, and followings are raised with this invention. The oxide (ITO) of an indium and tin, the oxide of cadmium and tin (CTO), The oxide of an aluminum oxide (aluminum<sub>2</sub> O<sub>3</sub>), a zinc oxide (ZnO<sub>2</sub>), zinc, and aluminum (AZO), A magnesium oxide (MgO), a thorium oxide (ThO<sub>2</sub>), the tin oxide (SnO<sub>2</sub>), A lanthanum trioxide (LaO<sub>2</sub>), a silicon oxide (SiO<sub>2</sub>), indium oxide (In<sub>2</sub> O<sub>3</sub>), They are a niobium oxide (Nb<sub>2</sub> O<sub>3</sub>), an antimony oxide (Sb<sub>2</sub> O<sub>3</sub>), a zirconium oxide (ZrO<sub>2</sub>), oxidization caesium (CeO<sub>2</sub>), titanium oxide (TiO<sub>2</sub>), a bismuth oxide (BiO<sub>2</sub>), etc. Moreover, you may use a transparent high refractive-index sulfide. If it illustrates concretely, zinc sulfide (ZnS), a cadmium sulfide (CdS), an antimony sulfide (Sb<sub>2</sub> S<sub>3</sub>), etc. will be raised.

[0017] Also of the above-mentioned transparent high refractive-index material, ITO, TiO<sub>2</sub>, and especially ZnO are desirable. ITO and ZnO A refractive index when it has conductivity is as high as about 2.0 to a visible region, and hardly has absorption in a visible region further in it. There is especially no limit in atomic composition of ITO, and the rate of the tin oxide to the whole ITO is usually 1 - 60 % of the weight. TiO<sub>2</sub> Although it is an insulator and it has slight absorption in a visible region, the refractive index to the light is as large as about 2.3.

[0018] The thickness of the transparent high refractive-index thin film layer (a) used by this invention is about 10-200nm. Moreover, when a transparent high refractive-index thin film layer (a) is included more than two-layer in the laminated structure of a layered product, the component of each transparent high refractive-index thin film layer (a) and the thickness may differ from \*\*\*\* conditions, respectively.

[0019] As a material of the metal thin film layer (b) used in this invention, the material with electrical conductivity sufficient as much as possible is desirable, and silver, gold, copper, palladium and platinum, or those alloys are used. Especially, a specific resistance is  $1.59 \times 10^{-6}$  (ohm and cm), and since it excels in electrical conductivity upwards most in all materials and the visible-ray permeability of a thin film is excellent, silver is used most suitably. However, silver lacks a stability, when it is made into a thin film, and it has the problem are easy to receive sulfuration and chlorination. In order to increase a stability for this reason, you may use silver, a golden alloy and silver, a copper alloy and silver, the alloy of palladium, or the alloy of silver and platinum instead of silver. There is especially no limit in atomic composition of a silver alloy, and the inclusion rate of the metal of the others to the whole silver alloy is usually 0.01 - 60 % of the weight. Although the visible light-transmission nature of a thin film is inferior as compared with silver, a specific resistance is  $1.67 \times 10^{-6}$  (ohm and cm), and since it excels in silver very much subsequently to electrical conductivity, copper can be used suitable for the metal thin film layer in this invention. Although the visible-ray permeability of a thin film is inferior to silver in gold as well as copper, since a specific resistance is excellent in  $2.35 \times 10^{-6}$  (ohm and cm), silver, and copper subsequently to electrical conductivity, it can use suitably as a metal thin film layer in this invention.

[0020] The thickness of the metal thin film layer (b) used by this invention is about 5-50nm. Moreover, when a metal thin film layer (b) is included more than two-layer in the laminated structure of a layered product, the component of each metal thin film layer (b) and the thickness may differ from \*\*\*\* conditions, respectively. The transparent substrate (A) used in this invention is transparent in the field of the light, and if it has the thermal resistance of 100 degrees C, it will not be restricted especially. However, in order to acquire the effect of this invention for a short time, it is more desirable to use the substrate which has the thermal resistance of 150 degrees C or more. Specifically, glass and a macromolecule Plastic solid can use it suitably. Since a limitation is in thermal resistance when a macromolecule Plastic solid is used although it is satisfactory even if it raises heat-treatment temperature to 150 degrees C or more when glass is used, heat-treatment temperature takes cautions.

[0021] If a desirable macromolecule Plastic-solid material is illustrated, a polyimide, a polysulfone (PSF), a polyether

sulfone (PES), a polyethylene terephthalate (PET), polymethylene methacrylate (PMMA), a polycarbonate (PC), a polyether ether ketone (PEEK), polypropylene (PP), etc. will be mentioned. Since it has the thermal resistance of 150 degrees C or more, a polyimide, a polysulfone, and a polyether sulfone can be used especially suitably. Moreover, since the effect of this invention can be acquired also about the other macromolecule Plastic solid by lengthening heat-treatment time also by heat-treatment below heat-resistant limit temperature, it is satisfactory in any way.

[0022] As long as the field which forms a transparent electric conduction layer is smooth to some extent, even if these macromolecules Plastic solid is tabular, it may be a film-like. Since it can form, without excelling in the mechanical strength upwards and contacting a transparent electric conduction layer front face to other matter, a tabular macromolecule Plastic solid can form the transparent conductivity thin film layer which has flat-surface homogeneity remarkably, and is used suitably [ a display etc. ] for [ which is asked for a mechanical strength and flat-surface homogeneity ] intended use.

[0023] Since the high polymer film has flexibility and can form a transparent electric conduction layer continuously by the \*\*\*\*\* rolling method, when this is used, it can produce a transparent conductivity thin film layered product efficiently, and can use it suitably. In this case, as for the thickness of a film, a 10-250-micrometer thing is usually used. Since flexibility runs short if the mechanical strength as a base material runs short of the thickness of a film and it exceeds 250 micrometers in less than 10 micrometers, it is not suitable for rolling round and using a film with a roll.

[0024] You may perform processing which raises the adhesion to the above-mentioned Plastic solid of the thin film layer which performs etching processing of sputtering processing, a corona treatment, a flame treatment, a UV irradiation, an electron beam irradiation, etc., and under coat processing to the front face beforehand, and is formed on this to these glass or a macromolecule Plastic solid. Moreover, before \*\*\*\*\*ing a thin film layer, you may perform protection-against-dust processing of solvent cleaning, ultrasonic cleaning, etc. if needed.

[0025] In addition, when the laminating of the thin film layer which consists of an element of another kind like this invention is carried out, the interface is not distinguished clearly and has usually produced counter diffusion. However, even if such counter diffusion arises, it is a domain which does not usually influence a performance. moreover, the suitable interlayer may also be boiled and included in order to raise the adhesion force between this thin film layer and a substrate or between laminating units Moreover, in order to raise gas barrier nature, you may form a gas barrier layer in the domain which does not spoil a performance. As location which can form a gas barrier layer, the principal plane which forms a layered product is on the substrate side by the side of reverse between the laminating units on a layered product electric conduction side and in a layered product. Furthermore, in order to raise abrasion-proof nature, a suitable hard-coat layer may also be included in the domain which does not spoil a performance. As a position which can form a hard-coat layer, the principal plane of a layered product is on the substrate by the side of reverse on a layered product electric conduction side.

[0026] What is necessary is to just be based on the technique in which a vacuum deposition method, the ion-plating method, the sputtering method, etc. are conventionally well-known to formation of a metal thin film layer, in this invention. Especially, a vacuum deposition method or the sputtering method is used suitably. At a vacuum deposition method, a desired metal can be used as a source of vacuum evaporatio, and a metal thin film layer can be formed simple by carrying out heating vacuum evaporatio by resistance heating, electron beam heating, etc. Moreover, when using the sputtering method, using the metallic material of a request at a target, inert gas, such as an argon and neon, can be used for sputtering gas, and a metal thin film layer can be formed using a DC-sputtering method or a RF-sputtering method. In order to raise a \*\*\*\*\* speed, the direct-current magnetron sputtering method and the RF magnetron sputtering method are used in many cases.

[0027] What is necessary is to just be based on the technique in which a vacuum deposition method, the ion-plating method, the sputtering method, etc. are conventionally well-known to formation of a high refractive-index thin film layer, in this invention. Especially, the ion-plating method or a reactive-sputtering method is used suitably. By the ion-plating method, resistance heating, electron beam heating, etc. perform vacuum deposition for a desired metal or a desired sintered compact in a reactant gas plasma. By the reactive-sputtering method, a desired metal or a desired sintered compact is used for a target, inert gas, such as an argon and neon, is used for reactive-sputtering gas, and sputtering is performed. For example, in forming ITO thin film, the oxide of an indium and tin is used for a sputtering target, and it performs direct-current magnetron sputtering in oxygen gas.

[0028] Although the heat-treatment in this invention is the meaning which prevents the reaction with the transparency conductivity thin film layered product of a circumference presence gas, and a substrate, and the irruption to them and it is desirable to be carried out under reduced pressure, even if it is performed under atmospheric pressure and pressurization, there is especially no problem. When processing under pressurization or atmospheric pressure

conditions, the suitable gas may be included in the heat-treatment ambient atmosphere. Although a suitable gas decreases the effect before and after the gas which increases the effect of heat-treatment before and after heat-treatment, the gas which does not affect the effect at all before and after heat-treatment, and heat-treatment, the property of the transparent conductivity thin film layered product after processing is the gas which is satisfactory at all on use here. When such a gas is illustrated concretely, they are air, a dry air, a steam, hydrogen, oxygen, a carbon dioxide, a carbon monoxide, methane, ethane, a propane, a heptane, nitrogen, ammonia, helium, an argon, a krypton, a xenon, etc.

[0029] What is necessary is just to decide on the temperature and time of heat-treatment according to the heat endurance of a substrate, and the demand property of a transparent conductivity thin film layered product. If the temperature of heat-treatment is 100 degrees C or more, in order to acquire the effect of this invention, there is especially no problem. However, since about [ 48h ] time is needed in order to acquire an effect when the temperature of heat-treatment is about 130 degrees C, in respect of practical use, it is not so desirable. If it is 150 degrees C or more in temperature of heat-treatment, since the effect of this invention can be acquired in about 20 minutes, it is more desirable. In addition, as an upper limit of the temperature of heat-treatment, it is below the heat-resistant limit temperature of the substrate to use.

[0030] Atomic composition of the transparent conductivity thin film layer formed by the above-mentioned technique can be measured by X-ray fluorescence, EPMA, a particle-induced-X-ray-emission method (PIXE), an Auger electron spectroscopy (AES), a Rutherford backscattering method (RBS), X-ray photoelectron spectroscopy (XPS), a vacuum-ultraviolet photoelectron spectroscopy (UPS), the infrared absorption spectroscopy, the Raman spectroscopy, secondary ion mass spectrometry (SIMS), the low-energy-ion-scattering spectroscopy (ISS), etc. Moreover, the depth orientation measurement of secondary ion mass analysis and the Auger electron spectroscopy can investigate the atomic composition in a layer, and a thickness.

[0031] In addition, there are followings as one view for explaining the phenomenon in this invention. For example, when an oxide is used for a transparent high refractive-index thin film layer, presence of the metallic oxide in a metal thin film layer can be considered as a cause by which field resistance and a visible light transmittance are greatly different widely with the value expected. Although a transparent high refractive-index thin film layer is generally \*\*\*\*ed by the sputtering method, an oxygen reactivity spatter is used in this case. In the case of transparent high refractive-index thin membrane layer \*\*\*\* to a metal thin film layer top, many of metals in a metal thin film layer oxidize by reactant spatter oxygen gas, and the point which exists as a metallic oxide is considered at it to be the cause which causes a fall of permeability, and elevation of resistance. In this invention, it is thought that the metal thin film layer which stimulates a reduction of the metallic oxide which exists in a metal thin film layer, and hardly contains an oxide by heat-treatment can be formed.

[0032] The example is the transparent conductivity thin film layered product which comes to carry out the laminating of the metal thin film layer (b) which consists of an ITO thin film layer (a) and silver on a transparent substrate (A) to A / order which becomes b/a. In case the laminating of the ITO layer (a) is carried out on a metal thin film layer (b) by the oxygen reactive-sputtering method, in order that oxygen ion may collide with the metal thin film layer (b) which consists of silver and may oxidize the atom of a metal thin film layer front face, many silver oxides are included in a metal thin film layer (b). By heat-treating this transparent conductivity thin film layered product under a condition 130 degrees C or more, the transparent conductivity thin film layered product which a silver oxide is returned for a short time, and hardly contains a silver oxide in a metal thin film layer (b) is manufactured.

[0033] The effect of this invention is considered to appear notably when more oxygen is included in the transparent high refractive-index thin membrane layer \*\*\*\* ambient atmosphere. As for the effect of this invention, the case where ITO layer (a) is formed in the bottom of a hyperoxia concentration ambient-atmosphere condition actually appears more notably. The hyperoxia concentration ambient atmosphere means concentration higher than an oxygen density from which the specific resistance of ITO formed becomes the minimum here.

[0034] Two kinds of silver oxides exist. One kind is a silver oxide (I) and ( $\text{Ag}_2\text{O}$ ). It is the cubic crystal of dark brown and a cuprite type structure is taken. A Gibbs energy is  $-11.2\text{kJmol}^{-1}$ , if it heats at 160 degrees C or more, it will decompose, and it emits oxygen. one more kind -- a silver oxide (II) and ( $\text{AgO}$ ) -- it is -- ashes -- although it is a black monoclinic-system crystal -- the substance --  $\text{AgI AgIII O}_2$  it is .  $\text{AgIII ****}$  -- four O -- a flat-surface top -- configuring --  $\text{AgI ****}$  -- two O has configured in the shape of a straight line It decomposes into silver and oxygen above 100 degrees C. A silver valence usually produces a monovalent compound. In the case of a silver oxide, a silver oxide (I) and ( $\text{Ag}_2\text{O}$ ) are produced. A silver oxide (II) and ( $\text{AgO}$ ) anodize silver or a silver oxide (I), or make a silver nitrate react with a caustic potash and persulfuric-acid potash, and are made. In this invention, it is expected that the

target silver oxide is a silver oxide (I) if the effect of this invention takes into consideration appearing notably by the origin of conditions with a heating temperature of 160 degrees C or more.

[0035]

[Example] Next, an example explains this invention concretely.

(Example 1) a transparent substrate -- (thin film layer (a) [40nm] silver thin film layer (b [10nm] which uses glass [0.8-1.0mm in Matsunami micro slide glass thickness] for A), and becomes it from the oxide of an indium and tin according to the following formation conditions at the principal plane of one of these) -- A/a/b / a -- the laminating was carried out to order and the transparent conductivity thin film layered product was formed Then, the difference between the electrical property with heating before and an optical property was investigated, heat-treating.

[0036] O The thin film layer which consists of an oxide of the formation technique (1) indium and tin (a)

- SnO<sub>2</sub> sintered compact (weight ratio 80:20) and technique:direct-current magnetron sputtering method and target:In<sub>2</sub>O<sub>3</sub>, and sputtering gas:argon oxygen mixed gas [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.018Pa]

- Sputtering power:130W and \*\*\*\* speed:14.5nm/min(2) silver thin film layer (b)

- Technique:direct-current magnetron sputtering law and target:silver (99.9% of purity)

- Sputtering gas:argon gas [the pressure of 0.6Pa]

- Set to - heating-time:each temperature every 10 degrees C in the sputtering power:100W and \*\*\*\*

speed:38.0nm/minO heat-treatment / heating ambient-atmosphere:atmospheric air, a heating pressure:ordinary pressure, and heating temperature:100-180 degree C, and it is the hold [0037] during 20 minutes, respectively. O Field resistance (omega/\*\*) was measured by the electrical property evaluation four probe method.

O All light transmissions were measured using optical characterization Hitachi make and the spectrophotometer U-3400. The value in 550nm was shown in the table.

[0038] The above result is hung up over drawing 9 . The effect of the field resistance fall by heat-treatment of a transparent conductivity thin film layered product and visible light-transmittance elevation appears from the neighborhood the heat-treatment temperature of about 100 degrees C so that drawing 9 may show. The effect becomes large gradually and becomes the maximum above 160 degrees C as heat-treatment temperature is raised.

[0039] (Example 2) Except the following points, the transparent conductivity thin film layered product was formed on the same conditions as an example 1, and heat treatment was performed for 20 minutes under the 180-degree C temperature condition. The electrical property and the optical property were compared before and after heat treatment. The thin film layer (a) formation condition and sputtering gas:argon oxygen mixed gas which consists of an oxide of an indium and tin [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- \*\*\*\* speed:12.6nm/min [0040] (Example 3) Except the following points, the transparent conductivity thin film

layered product was formed on the same conditions as an example 1, and heat-treatment was given for 20 minutes under the 180-degree C temperature condition. The electrical property and the optical property were compared before and after heat treatment.

- Instead of a silver thin film layer (b), the alloy [gold of silver and gold is :5 % of the weight] comparatively. It uses.

- \*\*\*\* speed:33.0nm of thin film layer of alloy of silver and gold/min [0041] (Example 4) It carried out on the same conditions as an example 3 except the following points.

The thin film layer (a) formation condition and sputtering gas:argon oxygen mixed gas which consists of an oxide of an indium and tin [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- \*\*\*\* speed:12.6nm/min [0042] (Example 5) It carried out on the same conditions as an example 3 except the following points.

- Instead of a silver thin film layer (b), the alloy [copper of silver and copper is :10 % of the weight] comparatively. It uses.

- \*\*\*\* speed:30.3nm of thin film layer of alloy of silver and copper/min [0043] (Example 6) It carried out on the same conditions as an example 5 except the following points.

The thin film layer (a) formation condition and sputtering gas:argon oxygen mixed gas which consists of an oxide of an indium and tin [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- \*\*\*\* speed:12.6nm/min [0044] (Example 7) It carried out on the same conditions as an example 3 except the following points.

- Instead of a silver thin film layer (b), the alloy [palladium of silver and palladium is :5 % of the weight] comparatively. It uses.

- \*\*\*\* speed:32.0nm of thin film layer of silver and alloy of palladium/min [0045] (Example 8) It carried out on the

same conditions as an example 7 except the following points.

The thin film layer (a) formation condition and sputtering gas: argon oxygen mixed gas which consists of an oxide of an indium and tin [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- Hang up the result \*\*\*\* speed: 12.6nm /, and more than min over (Table 1). However, about the example 1, the case with a heat-treatment temperature of 180 degrees C was chosen and hung up for the comparison with other examples.

[0046]

[Table 1]

表 1

熱処理	面抵抗 ( $\Omega/\square$ )		透過率 (%)	
	前	後	前	後
実施例 1	5. 9	4. 1	8 8	9 2
実施例 2	1 1. 4	4. 3	8 3	9 1
実施例 3	6. 8	5. 3	8 7	9 0
実施例 4	1 3. 2	5. 4	8 2	9 0
実施例 5	1 3. 0	7. 8	7 8	8 2
実施例 6	1 6. 2	8. 6	7 7	8 0
実施例 7	7. 5	6. 6	7 6	8 0
実施例 8	1 2. 2	6. 8	7 4	8 0

[0047] From Table 1, by heat-treating shows that field resistance and the light transmission of a transparent conductivity thin film layered product are improving in all the examples. This is remarkable when ITO thin film layer is formed under a hyperoxia concentration ambient-atmosphere condition like [ in the case of examples 2, 4, 6, and 8 ] as compared with the case where ITO thin film layer is formed like [ in the case of examples 1, 3, 5, and 7 ] by the origin of the conditions from which the specific resistance of ITO becomes the minimum.

[0048] (Example 9) The transparent conductivity thin film layered product was formed like the example 1 except having used the polyethylene-terephthalate film [125 micrometers in HSA (brand name) thickness by Teijin, Ltd.] for the transparent substrate. Except having made the conditions of heat treatment into the heating temperature of 130 degrees C, and 48h of heating times, it heat-treated like the example 1 and the electrical property and the optical property were compared before and after heat-treatment. The above result is hung up over Table 2.

[0049]

[Table 2]

表 2

熱処理	面抵抗 ( $\Omega/\square$ )		透過率 (%)	
	前	後	前	後
実施例 9	6. 2	4. 5	8 7	8 9

[0050] As shown in Table 2, when a macromolecule Plastic solid is used for a substrate, the effect of this invention can be acquired.

[0051] (Example 10) a transparent substrate (A) -- glass [0.8-1.0mm in Matsunami micro slide glass thickness] -- using it -- the formation conditions of the following [ principal plane / one's of these ] -- a titanium oxide thin film layer -- (a [40nm]) and a silver thin film layer -- (b [10nm]) -- A/b / a -- the laminating was carried out to order and the transparent conductivity thin film layered product was formed Then, it heat-treated, and it is before and after heating and the electrical property and the optical property were compared.

[0052] O Formation technique (1) titanium-oxide thin film layer (a)

- Technique:direct-current magnetron sputtering law and target:TiO<sub>2</sub> A sintered compact and sputtering gas:argon oxygen mixed gas [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- Sputtering power:130W and \*\*\*\* speed:10.3nm/min(2) silver thin film layer (b)

- Technique:direct-current magnetron sputtering law and target:silver (99.9% of purity)

- Sputtering gas:argon gas [the pressure of 0.6Pa]

- The sputtering power:100W and \*\*\*\* speed:38.0nm/minO heat-treatment / heating ambient-atmosphere:atmospheric air, a heating pressure:ordinary pressure, heating temperature:180 degree C, and heating-time:20 minute [0053] O Field resistance (omega/\*\*) was measured by the electrical property evaluation four probe method.

O All light transmissions were measured using optical characterization Hitachi make and the spectrophotometer U-3400. The value in 550nm was shown in the table.

[0054] (Example 11) a transparent substrate (A) -- glass [0.8-1.0mm in Matsunami micro slide glass thickness] -- using it -- the conditions as an example 10 that it is the same except the point of the following [ principal plane / one's of these ] -- it is -- a zinc-oxide thin film layer -- (a [40nm]) and a silver thin film layer -- (b [10nm]) -- A/b / a -- the laminating was carried out to order and the transparent conductivity thin film

O Formation technique (1) zinc-oxide thin film layer (a)

- Technique:magnetron DC-sputtering law and target:ZnO<sub>2</sub> A sintered compact and sputtering gas:argon oxygen mixed gas [the total pressure (an argon and oxygen) of 0.6Pa, and oxygen gas partial pressure 0.036Pa]

- sputtering -- the result power:130W and \*\*\*\* speed:14.1nm /, and more than min was hung up over Table 3

[0055]

[Table 3]

表 3

	面抵抗 (Ω/□)		透過率 (%)	
	前	後	前	後
実施例 1 0	6. 4	4. 5	8 8	9 3
実施例 1 1	6. 1	4. 4	8 6	9 1

[0056] As shown in Table 3, it is TiO<sub>2</sub> to a transparent high refractive-index thin film layer. Or ZnO<sub>2</sub> When it uses, the effect of this invention can be acquired.

[0057]

[Effect of the invention] this invention's field resistance is low by heating after a laminating the transparent conductivity thin film layered product which has a transparent high refractive-index thin film layer (a) and at least one layer (b) of metal thin film layers at least on a transparent substrate (A) in the laminating unit which consists of a substrate (A) side b/a on fixed temperature conditions, and the manufacture technique of the transparent conductivity thin film layered product with a high light transmission can be offered.

[Translation done.]

\* NOTICES \*

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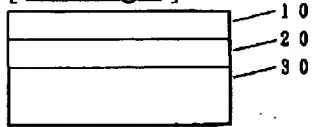
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
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- 3.In the drawings, any words are not translated.

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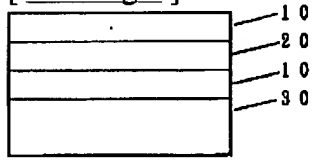
DRAWINGS

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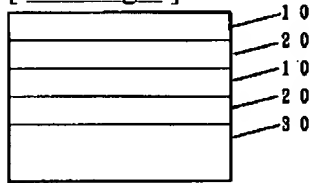
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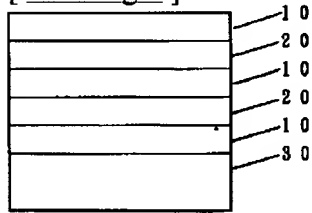
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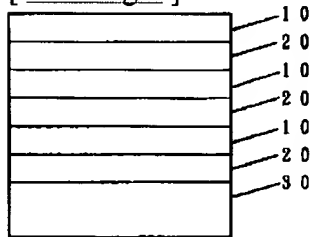
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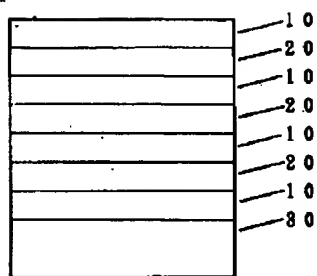
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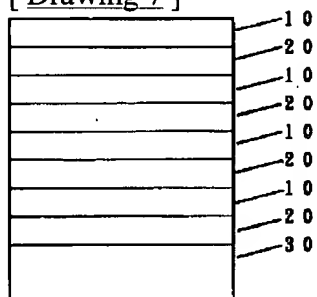
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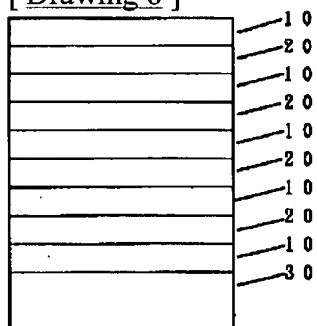
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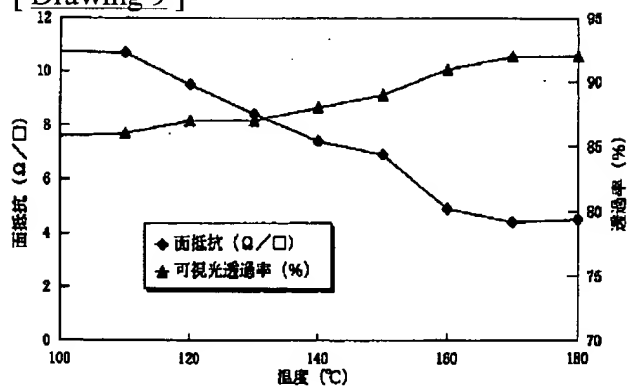
[ Drawing 7 ]



[ Drawing 8 ]



[ Drawing 9 ]



[Translation done.]